

Effects of Spherical Silica on the Properties of an Epoxy Resin System

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ABSTRACT: The spherical silica powders were prepared by using an oxygen–acetylene flame method. After spheroidization, a scanning electron microscope investigation revealed that the spheroidization efficiency of the powder was nearly 100%, XRD patterns indicated that the raw crystal silica became amorphous silica. In this study, composites of spherical silica and an epoxy resin were prepared with a homogenizer, followed by a stepwise thermal curing process. The thermal stability and thermal degradation behavior of the composites were studied by a thermogravimetric analyzer. Meanwhile, the effects of spherical silica powder on dynamic mechanical, coefficient of thermal expansion, and

mechanical properties of epoxy/silica composites were also investigated. The initial decomposition temperature and mechanical properties increased significantly after adding the spherical silica into the composite. The maximum properties of thermal stability and mechanical properties were observed when spherical silica accounted for 30% of the system. The thermal expansion had been significantly reduced by the addition of silica. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 648–653, 2011

Key words: spherical silica; composites; TG; thermal properties; mechanical properties

INTRODUCTION

Epoxy resins have relatively low volumetric shrinkage on polymerization, good thermal and dimensional stability, excellent moisture and chemical resistance, and superior electrical and mechanical properties.^{1,2} They are widely used as adhesives, coatings, and matrix materials for epoxy molding compounds in electronics such as semiconductor chips and printed circuit boards.³ Nowadays, research efforts on epoxy resins have focused on improving their mechanical properties, thermal stability,⁴ raising glass transition temperatures (T_g), lowering their dielectric constant,⁵ and coefficient of thermal expansion (CTE).⁶ Modification of epoxy resins is still necessary as some applications in the engineering field require better mechanical and thermal properties.

Using an inorganic filler to modify epoxy resins is one of the ways to overcome the problem successfully.^{7–11} Different types of particles such as carbon, clays, cellulose fiber, alumina, and silica have been

used to enhance the epoxy resin properties. Silica powder is the most widely used filler to enhance resins, especially in semiconductor encapsulates. With the development of the integrated circuit (IC) industry, there is a need for encapsulates with better mold-filling properties, making it essential to use spherical silica powders because of its excellent properties such as low CTE and high fluidity.¹² Spherical silica could be prepared by the plasma method,¹³ carbon electrode high-temperature process,¹⁴ sol–gel processing,¹⁵ and ethyl orthosilicate or silicon tetrachloride hydrolysis method.¹⁶ In this study, spherical silica powders used as fillers were prepared by using an oxygen–acetylene flame method.

On the basis of preparing spherical silica, the aim of this study was to clarify the effect of the different percentages of spherical silica on thermal stability, CTE, and mechanical properties and to find out the functional mechanism of silica powder and epoxy resins.

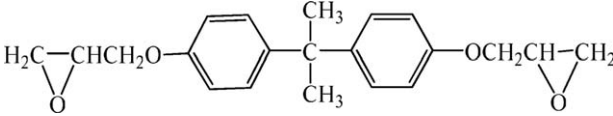
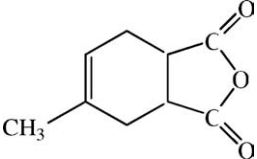
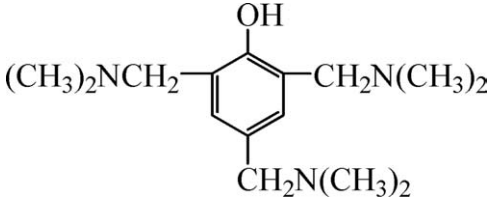
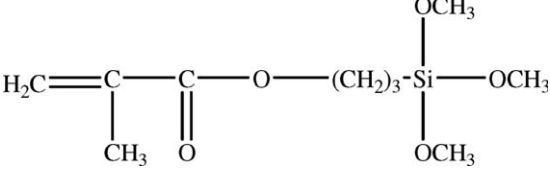
EXPERIMENTAL

Materials

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA; Araldite E-51,

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TABLE I
Chemical Structure of Organic Materials

Material	Chemical structure
E-51	
MeTHPA	
DMP-30	
KH-570	

Yueyang Baling Chemical, China.) with an epoxy equivalent weight of 450–500 g eq⁻¹. The curing agent was methyl tetrahydrophthalic anhydride (MeTHPA) from Jiaying Jinghua Chemical (China). The accelerator was 2,4,6-tri(dimethylaminomethyl)phenol (DMP-30) from Wuhan Chemical (China). The raw silica was purchased from Lianyungang Donghai Silica powder (China). The spherical silica powders were prepared from oxygen–acetylene flame spheroidization process. The spherical silica particle surface was modified by silane coupler (KH-570) that allowed polymerization directly with the resin matrix and prevented particle agglomeration. The structures of the used reagents in this article are shown in Table I.

Preparation of the spherical silica

The spherical silica powders were synthesized using the oxygen–acetylene flame method. Figure 1 shows the schematic of the apparatus. Major spheroidization parameters were carrier gas flow at 0.2 L min⁻¹, combustion supporting gas flow at 23 L min⁻¹, com-

bustible gas flow at 13 L min⁻¹, and a powder feeding rate of 15 g min⁻¹.

Preparation of the composites

Various amounts of silica were added into the DGEBA/MeTHPA/DMP-30 solutions to form mixtures. Resin, hardener and accelerator, was mixed at the stoichiometric proportion, 100 : 72 : 1. The rotor speed and stirring time were set at 800 rpm and 30 min, respectively. Then the mixtures were sonicated for 30 min in an ultrasonic bath to disperse the agglomerates. The composite paste was poured into a mould whose cavities were shaped. The samples were cured at 100°C for 2 h and then were post-cured for 2 h in an oven at 150°C and then cooled to room temperature.

Testing

The structure of the silica powders before and after spheroidization treatment was conducted in a RIGAKU D/Max-3B diffractometer using CuK_α

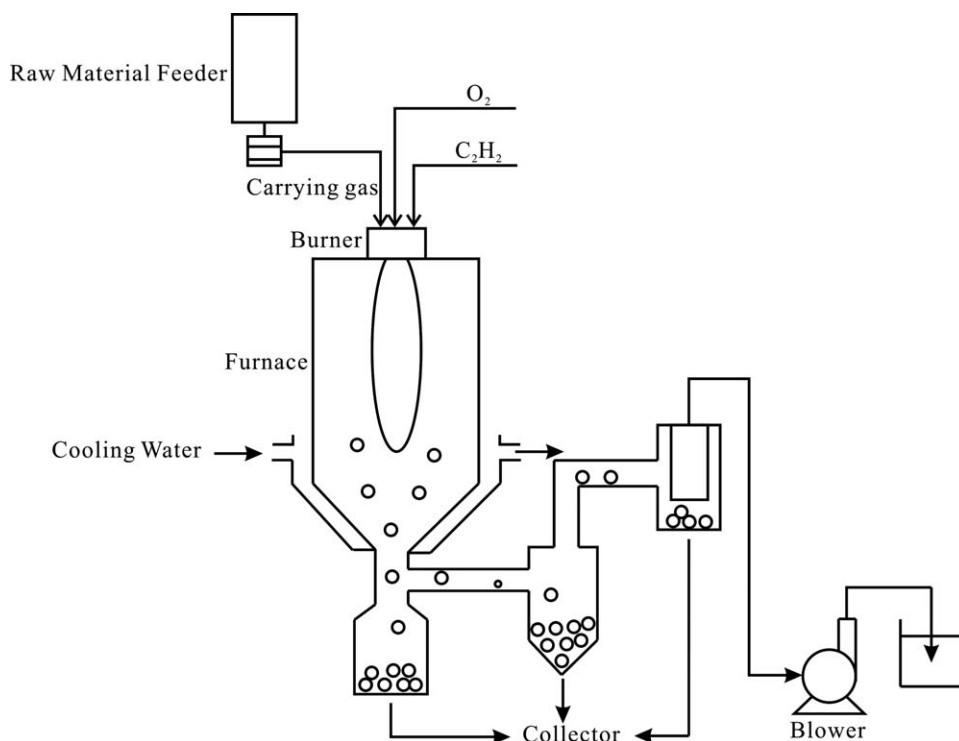


Figure 1 The schematic diagram of oxygen–acetylene flame spheroidization process.

radiation at a scan rate of $4^{\circ}\text{C min}^{-1}$. The accelerating voltage and the applied current were 30 kV and 20 mA, respectively. The morphology of spherical silica particle was observed by scanning electronic microscopy (Quanta 200, FEI, Holland) with an acceleration voltage of 30 kV.

Thermogravimetric (TG) studies were performed by differential scanning calorimetry and thermogravimetry (NETZSCH STA 449 C, Germany). The scans were performed at a rate of $10^{\circ}\text{C min}^{-1}$. Air flow at a rate of 50 mL min^{-1} was maintained throughout the experiments. A sample mass between 5.25 and 5.90 mg was chosen for each experiment, so that the amount of resin was approximately the same in all the experiments.

The CTE was measured with a NETZSCH (Germany) DIL402C device. The measurements were performed at a temperature range of $20\text{--}200^{\circ}\text{C}$ with a heating rate of $5^{\circ}\text{C min}^{-1}$.

The flexural properties were measured with a Testometric M500-25 kN tensile machine in accordance with ASTM D 790-86. Impact testing was performed with a Ray-Ran impact pendulum tester at the energy of 7.5 kJ, according to ASTM D 256-88.

RESULTS AND DISCUSSION

Characterization of the filler

The raw silica powders had a nonspherical shape and irregular morphology as shown in Figure 2(a).

After spheroidization by an oxygen–acetylene flame, the microscopic shapes of the particles were completely spherical, and the surface became smooth as shown in Figure 2(b), and the spheroidization efficiency of the powder was nearly 100%.

Figure 3 shows the X-ray diffraction (XRD) patterns of the silica powders before and after the spheroidization treatment. Compared with raw silica, the intensities of characteristic peaks of the spherical silica prepared by the oxygen–acetylene flame method were reduced and had broad peaks at around $2\theta = 21^{\circ}$ in the XRD spectrum; it indicated the transition of silica phase from crystalline to amorphous after the spheroidization treatment.

Characterization of epoxy/spherical silica composites

To quantify the actual effect of the filler, thermal stability parameters were calculated from the TG curves. For each sample, the minimum standard deviation of initial decomposition temperature (IDT) was observed at 3% mass loss. As shown in Figure 4, it can be observed that the thermal stability improved after being filled with spherical silica; this was because the spherical silica combined with the epoxy resin with a strong binding force, forming a cross-linked structure; moreover, the silica particles hinder the motion of the polymer molecular chain, preventing decomposition of the polymer.¹⁷

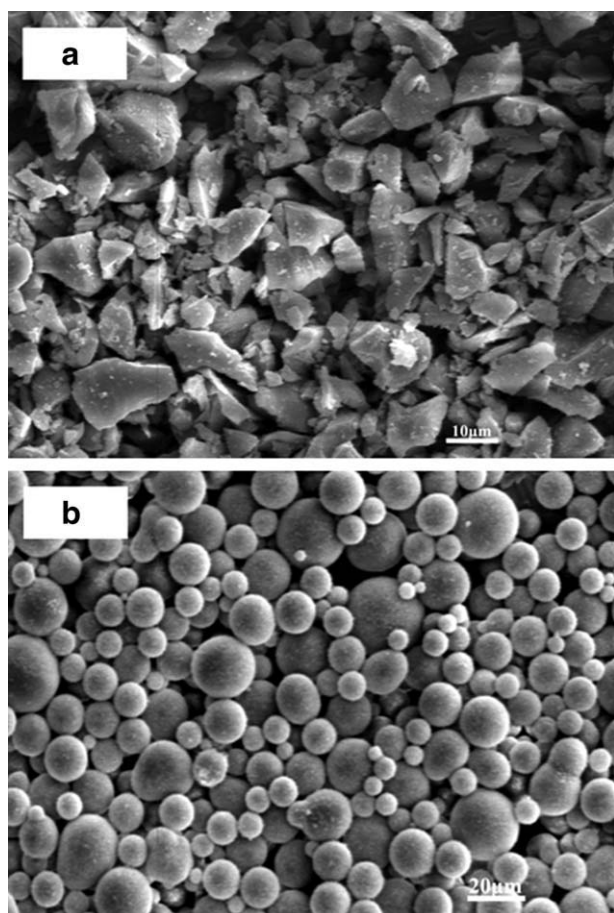


Figure 2 Scanning electron microscope images for the powders before (a) and after (b) spheroidization treatment.

At the same time, an IDT decrement was observed at 50% silica amount, which was attributed to the degree of dispersion of silica in the resin decreasing and the lower cross-linking grade due to the

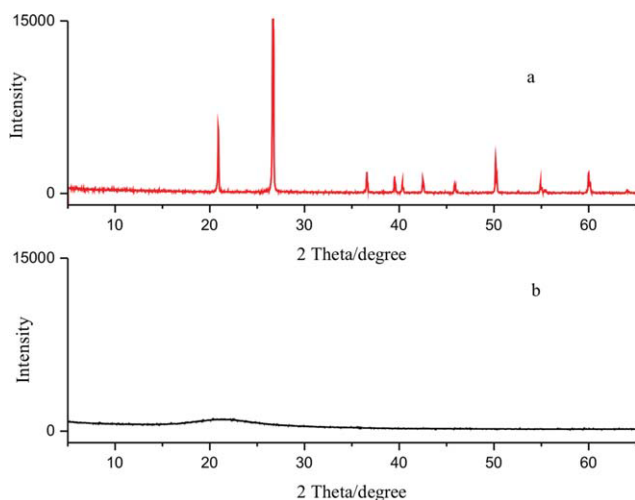


Figure 3 XRD patterns for the powders before (a) and after (b) spheroidization treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

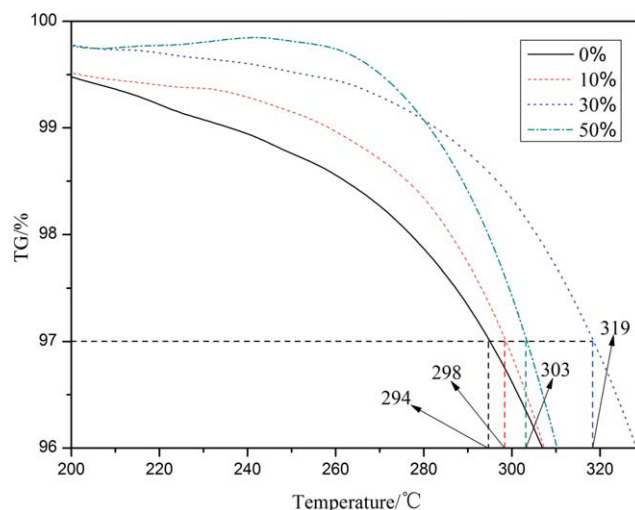


Figure 4 TG traces experimentally obtained with different silica contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased silica percentage. Some researchers found out that filler agglomeration is not an advantageous factor to enhance the thermal stability. Meanwhile, spherical silica particles subside in the epoxy resin; this phenomena results in the density of the cured compound being unequal. Only an extremely homogeneous particle distribution with the development of silica efficiently reinforces the polymer matrix.^{18,19}

Figure 5 shows the TG curves recalculated by subtracting the spherical silica filler content. It can be found that the curves look more alike with the filler content subtracted; it indicates that thermal degradation of the composites was only affected by spherical silica content.

To observe the degradation step and the maximum position of the composites, DTG curves were from TG data. As shown in Figure 6, 0% spherical

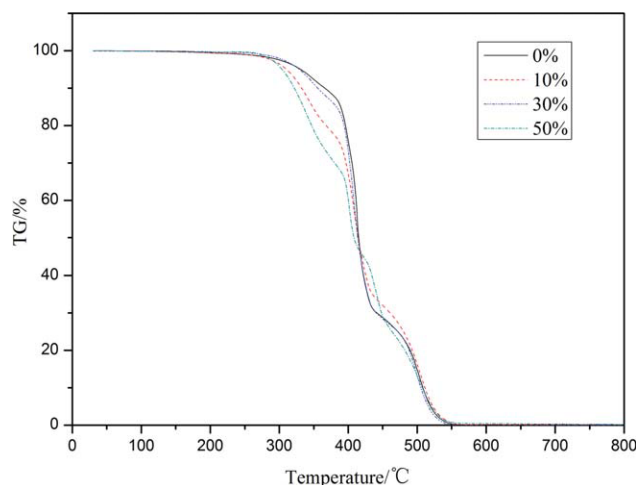


Figure 5 TG curves recalculated by subtracting the filler content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

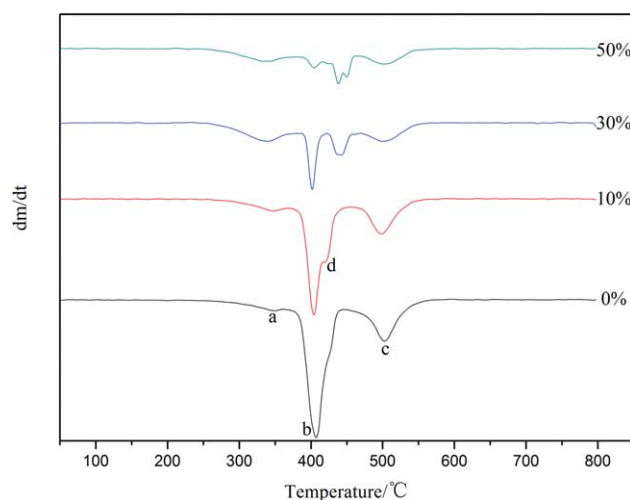


Figure 6 DTG curves obtained directly from the experimental TG data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silica composites only have three main degradation steps (a, b, and c). With the increasing of spherical silica content in composites, the maximum of the second stage not only displaces but it also splits. At that, the position of one of the maximums practically does not change, whereas others displace toward a high-temperature region: at silica concentration of 50%—approximately by 50°C for the maximum of the second stage possessing the highest temperature. This behavior suggests that degradation of the composites becomes complex because of spherical silica. It can also be explained on the basis that there is more hydrogen bonding between the organic and inorganic phases.

Figure 7 shows the linear coefficients of thermal expansion at temperature ranges both below and above T_g . It can be observed that CTE of composites decrease with an increase in the content of spherical silica. Depending on silica content and the tempera-

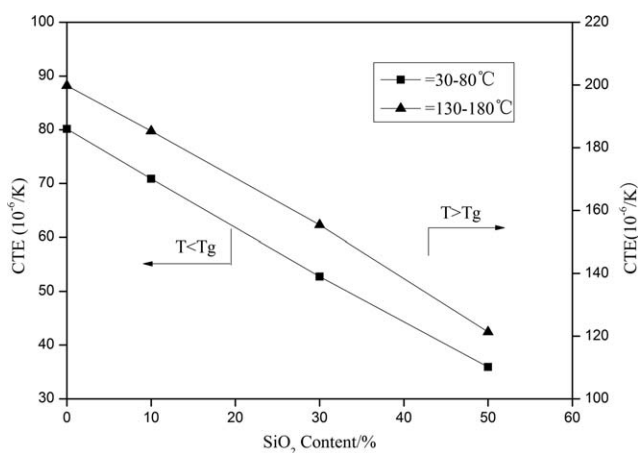


Figure 7 The CTE of epoxy-spherical silica as a function of the silica filler content.

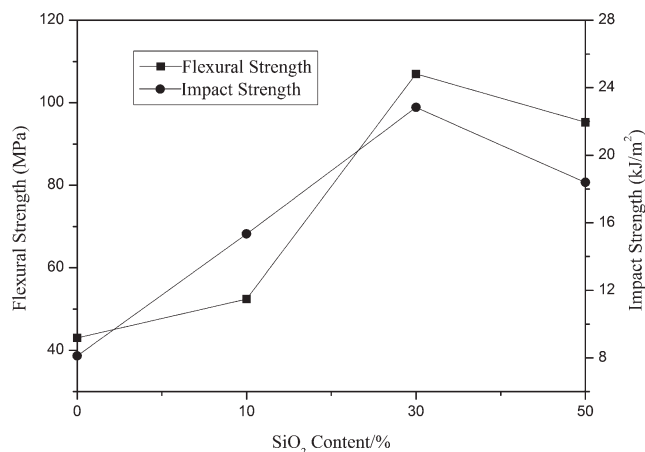


Figure 8 Flexural strength and impact strength of epoxy/spherical silica composites as a function of the silica content.

ture range, a significant depression in the CTE of up to 50% is observed (from 80.1 to $35.9 \times 10^{-6} \text{ K}^{-1}$ and from 199.8 to $121.3 \times 10^{-6} \text{ K}^{-1}$). This effect can be attributed to the considerably smaller CTE of the spherical silica ($5 \times 10^{-6} \text{ K}^{-1}$) in comparison to the significantly higher CTE of a neat polymer matrix. Meanwhile, by increasing the amount of spherical silica powder, the interface between the organic and inorganic phases increases, epoxy coating between inorganic filler particle is thinner than before, and the composites expanding become more difficult.

The mechanical parameters of the epoxy resin by adding spherical silica were investigated. The relative mechanical properties of the composites as well as the course of absolute values for flexural and impact tests are depicted in Figure 8. When compared with the neat resin, the addition of low content spherical silica at 10–30% results in an increase in flexural and impact strength. When the volume fraction of filler was 30%, the flexural strength and impact strength of composite came up to a maximum value of 107 MPa and 23 kJ m^{-2} , respectively. When the silica content was increased further, the mechanical properties of the composites decreased; this may be because of filler agglomeration leading to more internal stress. At the same time, the cross-point of the resin and silica particles also reduced, the composites fracturing need less energy.

CONCLUSIONS

In this article, high spheroidization efficiency spherical silica powders were prepared. The thermal stability, CTE, and mechanical properties of epoxy resin/spherical silica composites with different silica powder volume fraction content were investigated systematically. Thermal stability of spherical silica/

epoxy composites was evaluated by classical methods. It was found that thermal degradation of the resin was affected by the silica content. The composites have a maximum IDT of 319°C, when the volume fraction of filler was 30%. Some thermal stability improvements were explained by silica layer formation. Some worsening of the thermal stability was probably because of filler agglomeration. Compared to the nonfilled epoxy, spherical silica/epoxy composites have a lower CTE, and decreased with an increase in silica content, because spherical silica have lower CTE compared with neat polymer matrix. The flexural strength and impact strength of spherical silica/epoxy composites were increased after filling spherical silica. When the volume fraction of filler was 30%, the flexural strength and impact strength of composite came up to a maximum value of 107 MPa and 23 kJ m⁻², respectively.

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